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CONCERNING A FILING UNDER 35 U.S.C. 371

U.S. APPLICATION NO. (If known, see 37 CFR 1.55)

04/762396

INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/EP 99/05703	6 August 1999	7 August 1998

TITLE OF INVENTION: POLYMERS AND PLASTICS WITH LONG-LASTING ODOR AND THE USE THEREOF

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Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. /X/ This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.
2. / / This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.
3. /X/ This express request to begin national examination procedures (35 U.S.C.371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. /x/ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. /X/ A copy of the International Application as filed (35 U.S.C. 371(c)(2)).
  - a./X/ is transmitted herewith (required only if not transmitted by the International Bureau).
  - b./ / has been transmitted by the International Bureau.
  - c./ / is not required, as the application was filed in the United States Receiving Office (RO/USO).
6. X/ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. X/ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)).
  - a.X/ are transmitted herewith (required only if not transmitted by the International Bureau).
  - b./ / have been transmitted by the International Bureau.
  - c./ / have not been made; however, the time limit for making such amendments has NOT expired.
  - d./ / have not been made and will not be made.
8. X/ A translation of the amendments to the claims under PCT Article 19(35 U.S.C. 371(c)(3)).
9. / / An oath or declaration of the inventor(s)(35 U.S.C. 171(c)(4)).
- 10./ / A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).
- Items 11. to 16. below concern other document(s) or information included:
  - 11./ / An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
  - 12./ / An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
  - 13.X/ A FIRST preliminary amendment.  
/ / A SECOND or SUBSEQUENT preliminary amendment.
  - 14./ / A substitute specification.
  - 15./ / A change of power of attorney and/or address letter.
  - 16.x/ Other items or information.  
International Search Report  
International Preliminary Examination Report

09/762396

U.S. Appln. No. (If Known) INTERNATIONAL  
PCT/EP99/05703

ATTORNEY'S DOCKET NO.  
49256

	CALCULATIONS	PTO USE ONLY
17. /X/ The following fees are submitted		
BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5)):		
Search Report has been prepared by the		
EPO or JPO.....\$860.00	860.00	
International preliminary examination fee paid to USPTO		
(37 CFR 1.482).....\$750.00		
No international preliminary examination fee paid to		
USPTO (37 CFR 1.482) but international search fee paid		
to USPTO (37 CFR 1.445(a)(2)).....\$700.00		
Neither international preliminary examination fee		
(37 CFR 1.482) nor international search fee		
(37 CFR 1.445(a)(2)) paid to USPTO .....\$ 970.00		
International preliminary examination fee paid to		
USPTO (37 CFR 1.482) and all claims satisfied pro		
-visions of PCT Article 33(2)-(4).....\$96.00		
<b>ENTER APPROPRIATE BASIC FEE AMOUNT = \$ 860.00</b>		
Surcharge of \$130.00 for furnishing the oath or declaration		
later than // 20 // 30 months from the earliest		
claimed priority date (37 CFR 1.492(e)).		
<u>Claims</u>	<u>Number Filed</u>	<u>Number Extra</u>
Total Claims	16 -20	
Indep. Claims	1 -3	
Multiple dependent claim(s) (if applicable)	+270.	
<b>TOTAL OF ABOVE CALCULATION</b>		<b>= 860.00</b>
Reduction of 1/2 for filing by small entity, if applicable.		
Verified Small Entity statement must also be filed		
(Note 37 CFR 1.9, 1.27, 1.28).		
<b>SUBTOTAL</b>		<b>= 860.00</b>
Processing fee of \$130. for furnishing the English		
translation later than // 20 // 30 months from the		
earliest claimed priority date (37 CFR 1.492(f)).		
<b>TOTAL NATIONAL FEE</b>		<b>= 860.00</b>
Fee for recording the enclosed assignment (37 CFR 1.21(h)).		
The assignment must be accompanied by an appropriate cover		
sheet (37 CFR 3.28, 3.31) \$40.00 per property =		
<b>TOTAL FEES ENCLOSED</b>		<b>= \$ 860.00</b>
Amount to be		
refunded: \$		
Charged \$		

a./X/ A check in the amount of \$ 860. to cover the above fees is enclosed.

b./ / Please charge my Deposit Account No. \_\_\_\_\_ in the amount of \$ \_\_\_\_\_ to cover the above fees. A duplicate copy of this sheet is enclosed.

c./X/ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 11-0345. A duplicate copy of this sheet is enclosed.

**NOTE:** Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b) must be filed and granted to restore the application to pending status.

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## BOX PCT

Filed: August 6, 1999

PRELIMINARY AMENDMENT

Sir:

Prior to examination, kindly amend the above-identified application as follows:

IN THE CLAIMS

3. A process as claimed in claim 1 [or 2], wherein the odorant used comprises pheromones and/or ecomones.
4. A process' as claimed in claim 1 [any of claims 1 to 3], wherein the first plastic is mixed and allowed to swell with the odorant in a closed container.
5. A process as claimed in claim 1 [any of claims 1 to 4], wherein the first polymer material in the form of a powder is mixed with the odorant, allowed to swell, and then further processed with the second plastic in ground, powder or pellet form under high pressure and at about room temperature, and with heating to a temperature which is below the glass transition temperature of the second plastic, or with heating to a temperature which is above the glass transition temperature either of the first polymer material or of the second plastic.
6. A process as claimed in claim 1 [any of claims 1 to 5], wherein the first polymer material used comprises thermoplastics, thermoplastic elastomers, graft rubber, polymers based on renewable raw materials, or polymers or else polymer mixtures based on starch.
8. An odorant polymer or an odorant plastic obtained by the process as claimed in claim

1 [any of claims 1 to 7].

10. The use of the odorant polymer or plastic as claimed in claim 8 [or 9] for defense against animals.

11. A molding composition which comprises an odorant polymer or odorant plastic as claimed in claim 8 [or 9].

12. The use of the molding composition as claimed in claim 11 [or of the odorant polymer or plastic as claimed in claim 8 or 9] for altering and/or improving the odor properties of articles.

13. An article which comprises an odorant polymer or an odorant plastic as claimed in claim 8 [or 9 and/or a molding composition as claimed in claim 11].

15. The use of the article as claimed in claim 13 [or 14] for improving room air quality.

16. The use of the article as claimed in claim 13 [or 14] for defense against animal pests.

#### REMARKS

The claims were amended in the international preliminary examination. The claims have been amended further to eliminate multiple dependency and to put them in better form for U.S. filing. No new matter is included. A clean copy of the claims is attached.

Favorable action is solicited.

Respectfully submitted,

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## CLAIMS AS FILED IN THE PRELIMINARY AMENDMENT 99/05703

1. A process for preparing odorant polymers or plastics, in which a comminuted or fine-particle first polymer material is mixed with a desired odorant, allowed to swell for a predetermined period, and, after being allowed to swell with the odorant, is mixed with a second plastic, where the first polymer material differs from the second plastic and is selected from particulate cross-linked plastics or from thermoplastic elastomers which have rubbery properties, with a glass transition temperature  $T_g$  of  $\leq 0^\circ\text{C}$ , which is below the glass transition temperature of the second plastic.
2. The process as claimed in claim 1, wherein the odorant used comprises an odorant oil.
3. A process as claimed in claim 1, wherein the odorant used comprises pheromones and/or ecomones.
4. A process' as claimed in claim 1, wherein the first plastic is mixed and allowed to swell with the odorant in a closed container.
5. A process as claimed in claim 1, wherein the first polymer material in the form of a powder is mixed with the odorant, allowed to swell, and then further processed with the second plastic in ground, powder or pellet form under high pressure and at about room temperature, and with heating to a temperature which is below the glass transition temperature of the second plastic, or with heating to a temperature which is above the glass transition temperature either of the first polymer material or of the second plastic.

6. A process as claimed in claim 1, wherein the first polymer material used comprises thermoplastics, thermoplastic elastomers, graft rubber, polymers based on renewable raw materials, or polymers or else polymer mixtures based on starch.

7. A process as claimed in claim 6, wherein the second plastic is selected from polylactic acid, polyurethanes, polyamides, polyesters, polyester-amides, and polybutylene terephthalates, or from polymers, copolymers, block copolymers, triblock copolymers, or graft copolymers of styrene, butadiene, acrylonitrile, (meth)acrylate, or of acrylic esters, and also mixtures of these with polycarbonates.

8. An odorant polymer or an odorant plastic obtained by the process as claimed in claim 1.

9. An odorant polymer or odorant plastic as claimed in claim 8 in pellet form.

10. The use of the odorant polymer or plastic as claimed in claim 8 for defense against animals.

11. A molding composition which comprises an odorant polymer or odorant plastic as claimed in claim 8.

12. The use of the molding composition as claimed in claim 11 for altering and/or improving the odor properties of articles.

13. An article which comprises an odorant polymer or an odorant plastic as claimed in

claim 8 .

14. An article as claimed in claim 13 in the form of a plastic molding or a semifinished product.

15. The use of the article as claimed in claim 13 for improving room air quality.

16. The use of the article as claimed in claim 13 for defense against animal pests.

## AS ORIGINALLY FILED

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5        Polymers and plastics with long-lasting odor and the use thereof

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10        The invention relates to a process for preparing odorant polymers and plastics, to the odorant polymer or the odorant plastic itself, and also to a molding composition and an article which comprise the odorant polymer or the odorant plastic.

15        For some time the prior art has included efforts to prepare odorant plastics. Considerable practical problems arise here. If the intended plastic is mixed with the required amount of a desired odorant, such as a perfume, and the mixture is then  
20        processed to give moldings, most of the odorant evaporates or is thermally degraded. In relation to the proportion of the odorant which actually remains within the plastic, there is also the risk that the odorant will separate out from the plastic once the latter has cooled and solidified. This results in migration of the odorant to the surface of the solidified plastic, giving the surface a "greasy",  
25        unsightly and disfigured appearance. This process also inevitably results in high losses of the expensive odorant.

30        In order to eliminate these disadvantages, it is known in the prior art, via DE-A-16 94 055, that a silicon dioxide powder as carrier material can be mixed  
25        with a liquid odorant until the resultant mixture forms small clumps. Further silicon dioxide powder with a lower apparent density than the silicon dioxide initially used is added to these clumps, giving small clumps of dimensions not greater than 0.05 mm. These are then mixed with the plastic.

30        A disadvantage of this process is that the plastic processed in this way comprises an inorganic solid which can adversely affect the physical properties of the plastic, for example impact strength and transparency.

35        DE-A-37 21 916 begins with pulverulent porous carrier materials whose origin may be either inorganic or organic, in the form of plastics or of plastics mixtures.



The desired odorant is adsorbed onto the porous carrier material and mixed with a plastic for further processing by, for example, extrusion.

During the processing of the plastics the odorant diffuses into the polymer matrix.

- 5 A disadvantage here is that this diffusion of the odorant into the polymer matrix during processing can also lead to loss of the odorant, since the porosity of the particular carrier material means that the odorant is adsorbed in the pores of the carrier, rather than absorbed.
- 10 It is an object of the present invention, taking this prior art as a starting point, to provide a process which allows cost-effective preparation of odorant polymers, in particular of odorant plastics with long lasting odor, and to provide these odorant polymers and this odorant plastic.
- 15 We have found that this object is achieved by means of a process in which a comminuted or fine-particle first polymer material, in particular a plastic, is mixed with a desired odorant, allowed to swell for a predetermined period, and then further processed under a predetermined pressure and at a predetermined temperature. Since the comminuted or fine-particle first polymer material is mixed
- 20 and allowed to swell with the desired odorant for a predetermined period, the odorant can enter into every one of the particles of the first polymer material. The polymer particles are genuinely loaded with the odorant. Correspondingly, for the purposes of the present invention swelling is the absorption of the odorant into the polymer matrix or, respectively, the polymer network of the first polymer, which is
- 25 used as a carrier. A precondition for this is that the distribution of the odorant in the first polymer material is uniform. In the case of macroporous materials - as in the prior art - what is obtained is merely pores charged with odorant, without any loading of the polymer skeleton. If the odorant has sufficient thermal stability, the resultant odorant polymer or plastic can be further processed in a usual manner by
- 30 melting followed by homogenization. Particular further processing methods for odorants of relatively low thermal stability are given at a later stage in this text.
- In one preferred embodiment of the process of the invention, after the first polymer material has been allowed to swell with the odorant it may be mixed with a second
- 35 plastic and then melted and then homogenized. This gives a compact material which comprises the odorant polymer material together with the second plastic, the

macroscopic distribution being approximately uniform. For the purposes of the present invention, the first and second material are differentiated by referring to the first as the polymer material, the carrier material, and the second as the plastic, the objective here being to make it clear that the first polymer material may be, but  
5 does not have to be, a thermoplastic.

The second plastic may likewise have been comminuted, but this is not an essential requirement.

10 The first polymer material and the second plastic may be identical or differ from one another. If the first polymer material is identical with the second plastic, then for the purposes of the present invention the second plastic may also be a polymer material which is not a plastic. This method gives an odorant polymer. If the first  
15 polymer material, which serves as actual carrier material for the odorant, differs from the second plastic, the first polymer material in particular comprises a plastic in the form of a particulate, crosslinked plastic or of an elastomer, which may also have rubbery properties, with a glass transition temperature  $T_g$  below the glass transition temperature  $T_g$  of the second plastic, preferably  $0^\circ\text{C}$  or below, particularly preferably below  $-10^\circ\text{C}$ .

20 The way in which first polymer materials of this type can be saturated with the particular odorants used is that they form a microscopically small network which absorbs the odorants, whereupon the odorants swell the network. The odorant used may be an odorant oil. A particular use of the polymers or plastics prepared by the  
25 process of the invention becomes possible if the odorants used comprise pheromones and/or ecomones. Plaques coated or saturated with pheromones have hitherto been used with promising results for controlling insects. Since pheromone traps of this type are mostly employed in the open, these products are exposed to weathering and therefore have to be frequently replaced since the active ingredient  
30 is leached out. By employing the process of the invention it is possible to incorporate these odorants into the particular plastic provided so that the odorants are protected from the effects of weathering and can be used in the form of boards, plaques, or other moldings with a lasting odor. The process of the invention for preparing odorant polymers or plastics is therefore not restricted to those polymers  
35 or plastics providing an odor detectable by the human smell, but also encompasses

odorant polymers or plastics whose odor can be detected only by the sensitive olfactory systems of animals, in particular of insects.

- 5 The mixing of the first polymer material with this odorant or odorant oil may be carried out in a closed container. This ensures that all of the odorant oil is available for the loading of the first polymer material, rather than being dissipated into the environment. Examples of materials suitable for preparing the powder of the first polymer material are spray-dried dispersions of polymer or of plastic.
- 10 Depending on the nature of the odorant used, in particular on its thermal stability, the first operation consisting of mixing the first polymer material in powder form with the odorant and allowing it to swell may be followed, in the further operation to form the odorant polymer or plastic, by process modifications individually matched to the odorant. The second plastic here may be used in ground, powder, or
- 15 pellet form.

- 20 In the case of odorants with very low thermal stability, the method of further processing may be that once the first polymer material has been allowed to swell it is mixed with the second plastic at high pressure at about room temperature or by way of slight heating to below the glass transition temperature  $T_g$  of the second plastic, preferably to just below  $T_g$ . The second plastic material used is then preferably one which melts at a low temperature, the phenomenon of cold flow being utilized. The second plastic may be the same as the first polymer material but may also differ therefrom. A procedure such as that described is particularly
- 25 suitable for pheromones or ecomones in general.

- 30 In the case of odorants which have little or no sensitivity to high temperatures, once the first polymer material has been allowed to swell it may be mixed with the second plastic again at high pressure and with heating to a temperature which is above the glass transition temperature  $T_g$  either of the first polymer material or of the second plastic, preferably just above  $T_g$  in each case.

- 35 However, in the case of odorants which have no particular sensitivity to high temperatures it is quite possible to provide conventional pressure conditions and temperature conditions during processing, e.g. by extrusion. The mixture of the odorant-loaded first polymer powder and the second plastic, e.g. in the form of

pellets, may then be melted and homogenized in a mixing assembly at atmospheric pressure and at an elevated temperature. The melting in the mixing assembly may, for example, be carried out in an extruder or kneader. After homogenization, the resultant melt may be pelletized and further processed by the usual methods of processing for thermoplastic molding compositions.

- Materials preferably used as first polymer material are thermoplastics, thermoplastic elastomers, graft rubber, polymers based on renewable raw materials, or polymers or polymer mixtures based on starch. It is particularly preferable for the first polymer material to be selected from polylactic acid, as an example of a polymer based on renewable raw materials, polyurethanes, polyamides, polyesters, or polybutylene terephthalates, or polymers, copolymers, block polymers, triblock copolymers, or graft copolymers of styrene, butadiene, acrylonitrile, (meth)acrylate, or acrylic esters. The abovementioned materials are also suitable for use as second plastic, and in that case it is also possible to use mixtures of these with polycarbonates. Examples of the abovementioned polymers, copolymers or triblock copolymers are polystyrene (PS), in particular here impact-modified polystyrene, polybutadiene, polyacrylates, polymethyl methacrylates (PMMA), acrylonitrile-butadiene-styrene copolymers (ABS), acrylonitrile-styrene-acrylate copolymers (ASA), styrene-acrylonitrile copolymers (SAN), styrene-butadiene copolymers (SBR), acrylonitrile-butadiene copolymers (NBR), and styrene-butadiene-styrene triblock copolymers (SBS). Good results are also achieved using ground superabsorber material.
- The first polymer material may be in the form of a dewatered emulsion polymer, for example, obtained either by spray drying or by coagulation and drying. Fine-particle polymer powders obtained by precipitation from solutions are also highly suitable as first polymer material.
- The invention also provides the odorant polymer or the odorant plastic itself, obtained by the process of the invention. For simplicity, the text below refers to odorant plastics, and this is intended to include the possibility that the materials used produce an odorant polymer which is not a plastic. The odorant plastic may be in pellet form and an example of its use is in defense against animals. For the purposes of the present invention, animals may be pests, in particular including insects. However, defense against animals includes the repelling of domestic

animals, such as dogs, cats and other small animals from places which they would like to foul but where this fouling is undesirable. Pellets made from the odorant plastic may preferably be used here, and particularly preferably pellets made from biodegradable plastics and loaded with the appropriate odorants which are known  
5 per se and repel the animals. Examples of these biodegradable plastics are polymers based on renewable raw materials, for example polylactic acid, and polymers and polymer mixtures based on starch or based on synthetic materials, for example based on polyesteramides or on branched polyesters. The advantage of using the odorant plastic of the invention is that the active ingredient is dissipated  
10 over a long period and cannot be removed from the plastic even by rain.

The invention further relates to a molding composition which comprises an odorant polymer of this type or an odorant plastic of this type. Depending on the proportion of odorant in the finished plastic, which may be in the form of pellets, for example,  
15 this may also be used as a masterbatch. The relatively high proportion of odorant may be achieved, for example, by altering the mixing ratio of first polymer material and second plastic.

The invention also relates to the use of the molding composition which comprises  
20 an odorant polymer or an odorant plastic, or the use of the odorant polymer or plastic itself for altering and/or improving the odor properties of articles. There is a wide variety of applications available here, and particular advantage is given by those which conceal the unavoidable unpleasant intrinsic odors of plastics in a wide variety of applications. An example which may be mentioned here is the  
25 interior of motor vehicles in which components produced from plastic, for example dashboard supports, center consoles, trim films, etc. can have a strong odor of the plastic when they are new. Using the odorant plastics or the molding compositions prepared therefrom, this unpleasant odor can be concealed. Since the skilled worker is aware of a very broad range of very varied odorants, all of which can be  
30 incorporated into the plastic by the process of the invention, a varied range of possibilities is available to automobile manufacturers. Examples which may be mentioned here are plastics with the odor of leather, fresh air, flowers, forest or perfume.

35 Another possible application consists in concealing unpleasant intrinsic odors of construction materials, for example in the window frame sector or the baseboard

sector. Here, too, in the first weeks after completion the intrinsic odors occurring are regarded as unpleasant and may be concealed, for example using a citrus odor.

5 Other articles manufactured from plastic, such as vacuum cleaner housings or plastic parts in refrigerators, may have an unpleasant odor of the plastic from which they have been produced, such as an ABS plastic or an impact-modified polystyrene. These odors, too, may be concealed by a wide variety of desired types of odor, using odorant plastics.

10 The invention also provides an article which comprises the odorant polymer or the odorant plastic and/or comprises the molding composition in which the odorant polymer or the odorant plastic is present. This article may be a plastic part or a semifinished product, for example an injection molded article, or a film, sheet, pipe, or profile. There are many uses for the article, which has at least some inbuilt  
15 odor due to the odorant polymer or plastic present therein. Firstly, it may be used for the uses described above for the odorant polymer or the odorant plastic and for the molding composition which comprises the odorant polymer or odorant plastic. Secondly, however, it may be used for improving room air quality. It then acts as an odor dispenser, and it is advisable here to avoid any excessive proportion of the  
20 odorant present in the plastic, so that the article generates an odor which is discrete and only just detectable when in use in office areas or other living areas. However, a higher proportion of the odorant may be indicated if the article used as odor dispenser is employed in the sanitary sector. If the article has been produced by injection molding, it may advantageously be given any desired shape. For example,  
25 it is possible to produce lemons with the odor of lemons or coniferous trees which give out an odor of spruce needles, or any desired other article with its associated odor characteristics. These odorant articles are therefore also suitable as decorative articles.

30 Another possibility is to incorporate the odorant plastic into articles in daily use, such as household articles, telephones, computer casings, etc. The corresponding odorants may be selected so as to provide a motivation to purchase, or to generate a general feeling of wellbeing, or else even to increase the ability to concentrate. It is also possible for promotional items, such as ballpoint pens or other small  
35 products, to be provided with a customer-specific odor, these articles comprising the odorant plastic or the molding composition which comprises the odorant

plastic. In addition, it is possible to produce odorant greeting cards, CD packaging, cassette packaging, telephone cards, or chip cards.

If the articles are produced in the form of sheeting, they may be used as packaging  
5 films, as self-adhesive odorant labels for refrigerators, for example to eliminate  
fishy odors, or for wardrobes or other storage boxes. It should be emphasized that  
the selection of the appropriate odorant also allows long lasting defense against  
pests. For the purposes of the present invention, the term pest has a wide meaning,  
including insects and also small animals, such as mice, rats, martens, etc. Use of  
10 the appropriate odorants permits appropriate repellent cable-insulation materials to  
be used in electrical engineering. It is not just cable-insulating material which may  
be brought into consideration here, but any construction material liable to attack by  
small animals. In relation to the defense required against insect pests, mosquitoes  
and ants are worthy of consideration, as are various moth species.

15 Examples of the uses mentioned for the odorant plastic, or the molding  
composition or article comprising the odorant plastic are so varied that they can  
only be illustrated here by way of example. The use can also be extended to any  
desired other sectors of daily life. For example, selection of a suitable odorant  
20 plastic also permits the production of toys with a variety of aromas.

The invention will be described in more detail below by way of examples.

#### Example 1:

25 The first polymer material is composed of a spray-dried polybutadiene and  
polyacrylate rubber. 200 g of this dried rubber was placed in a 1 000 ml screw-top  
glass container and mixed with 10 or 20% of the odorant citral or citronellol. The  
glass containers were then rolled on a roller bed for 48 h. This mixed the odorant  
30 uniformly into the rubber.

The rubber treated in this way was blended firstly with a styrene-acrylonitrile  
polymer with a melt index MVI (220°/10 kg) of 62 g/10 min, at a concentration of  
10 or 20%, and secondly with nylon-6 with a melt index MVI (275°/5 kg) of  
35 120 g/10 min, in the same mixing ratio. Then each rubber-pellets mixture was

compounded in an extruder with contrarotating screws. The machine parameters here were set as follows:

	Screw rotation rate:	200 rpm
	Temperatures:	Feed: 30°C,
5		Processing unit: 220°C
	Throughput:	1.5 kg/h

The experiments carried out under Example 1 are shown in Table 1.

10 **Example 2:**

In this example the first polymer material is composed of a graft rubber dried in a fluidized-bed dryer and prepared as described in DE-B-24 27 960.  $\text{MgSO}_4$  was used for precipitation, followed by preliminary dewatering to a water content of  
15 about 28% by centrifuging. 100 parts of this graft rubber were treated with 25 parts of citronellol and mixed as described in Example 1.

40 parts of the graft rubber pretreated in this way were intimately mixed with 60 parts of a styrene-acrylonitrile copolymer melt (SAN) at 230°C in an extruder  
20 with corotating screws. The acrylonitrile content in the SAN melt was 35%. This gave a melt with a strong lemon odor, and the melt was used to produce moldings, such as plaques and bars, which continued to have a strong lemon odor. Films were also produced.

25 The resultant moldings were subjected to an odor test at intervals of a number of months. Even after a storage time of 10 months here, it was still possible to detect a pronounced lemon odor.

**Example 2a:**

30

The mixture of Example 2 made from the graft rubber and the citronellol was mixed with SAN in such a way that only about 30% of the odorant-saturated graft rubber was present in the finished mixture. This mixture, too, had a strong lemon odor.

35



The odor test was again undertaken over a period of a number of months. After 10 months here there was still a discrete, pleasant fruity odor.

Examples 2-1 to 2-7:

5

Odorant plastics of the invention were prepared as described in Example 2 from other polymer materials and plastics given in Table 2, using the odorants also given in that table.

Table 1:

Experiment	1st Polymer material	Odorant	Amount %	2nd Plastic material	Con-stituent amount %	Color
1	Polybutadiene	Citral	10	Styrene-acrylonitrile polymer	10	Slightly yellowish
2	Polybutadiene	Citral	10	Styrene-acrylonitrile polymer Nylon-6	20	Slightly yellowish
3	Polybutadiene	Citral	20	Nylon-6	10	Brownish yellow
4	Polybutadiene	Citral	20	Nylon-6	20	Brownish yellow
5	Polybutadiene	Citronellol	10	Styrene-acrylonitrile polymer	10	Very slightly yellowish
6	Polybutadiene	Citronellol	10	Styrene-acrylonitrile polymer Nylon-6	20	Very slightly yellowish
7	Polybutadiene	Citronellol	20	Nylon-6	10	Very slightly yellowish
8	Polybutadiene	Citronellol	20	Styrene-acrylonitrile polymer	20	Very slightly yellowish
9	Polyacrylate	Citral	10	Styrene-acrylonitrile polymer Nylon-6	10	Slightly yellowish
10	Polyacrylate	Citral	10	Nylon-6	20	Yellowish
11	Polyacrylate	Citral	20		10	Yellow-orange
12	Polyacrylate	Citral	20		20	Yellow-orange
13	Polyacrylate	Citronellol	10	Styrene-acrylonitrile polymer	10	Slightly yellowish
14	Polyacrylate	Citronellol	10	Styrene-acrylonitrile polymer Nylon-6	20	Slightly yellowish
15	Polyacrylate	Citronellol	20	Nylon-6	10	Slightly yellowish
16	Polyacrylate	Citronellol	20	Nylon-6	20	Slightly yellowish

\*) Relates to the proportion of the first loaded polymer material in the mixture with the second plastic

Table 2:

No.	1st Polymer material	Odor	Amount introduced % by weight	2nd Plastic	Mixing ratio polymer: plastic	Remarks
2-1	Polybutadiene-g-SAN	Nerolidol*	10	SAN	30:70	Floral odor, reminiscent of green timber
2-2	Polybutadiene-g-SAN	Phytol*	15	SAN	30:70	Sweet floral odor
2-3	Polybutadiene-g-SAN	Hydroxyciol*	20	ABS	20:80	Floral; peony
2-4	Polybutadiene-g-SAN	Geranyl acetate* 70-30	15	ABS	25:75	Fresh rose odor
2-5	Polybutadiene-g-SAN	Alfa-Ionon-100*	10	ABS	30:70	Floral/woody
2-6	Polybutadiene-g-SAN	2-Phenylethanol	15	PMMA	40:60	Transparent, floral odor, rose
2-7	Polybutadiene-g-SAN	N,N-Diethyl-m-toluamide	15	SAN	30:70	Repels mosquitoes

\*) Chemical name in Table 2a

Table 2a:

Odorant BASF trade name	Chemical name
Nerolidol	3,7,11-Trimethyldodecatrien-3-ol
Phytol	3,7,11,15-Tetramethylhexadec-2-en-1-ol
Hydroxyciol	3,7-Dimethyloctane-1,7-diol
Geranyl acetate	Mixture of 70% geranyl acetate and 30% neryl acetate
Alfa-Ionon 100	4-(2,6,6-Trimethyl-2-cyclohexen-1-yl)-3- buten-2-one

**Example 3**

5

The materials and odorants given in Table 3 were used to repeat the preparation of the mixture of Example 1 from the graft rubber and the odorant oil. The materials mentioned under 3-11 to 3-14 are fully biodegradable polymers. The odorants used are sensitive to high temperatures.

10

Once each odorant had been mixed into the first polymer material, this material was mixed with each of the pulverulent or pelletized plastic given and compressed into a mold under mild conditions, with heating to just above the glass transition temperature  $T_g$  of the thermoplastic used.

15

As an alternative to this, the mixtures resulting from the first polymer material and the second plastic were processed between heated rolls to give films.

In these versions of the process the processing temperatures selected were below  
20 the usual temperatures for extrusion, the extent about 50 to 150°C.

Table 3:

No.	1st Polymer material	Odorant	% by weight	2nd Plastic	Mixing ratio polymer: plastic	Remarks
3-1	Polybutadiene-g-SAN	Citronellol	20	SAN	10:90	Fruity odor, lemon aroma
3-2	Polybutadiene-g-SAN	Linalyl acetate*	10	ABS	25:75	Fruity; bergamot
3-3	Polybutadiene-g-SAN	Ethyl isovalerate	15	ABS	20:80	Fruity, grape, apple
3-4	Polybutadiene-g-SAN	Isoamyl acetate*	20	ABS	15:85	Fruity, peach, banana
3-5	Polybutyl acrylate-g-SAN	Acetoin*	15	ASA	10:90	Odor of butter, cream
3-6	Polybutyl acrylate-g-SAN	Cyclohexylethyl acetate	15	SAN	25:75	Fruity, apple, raspberry
3-7	Polybutadiene-g-MMA	Tetrahydrofuralol*	10	SAN/PMMA	30:35:35	Translucent, floral, slightly woody
3-8	Polybutyl acrylate-g-SAN	2,6-Dimethyl-2-heptanol N,N-Diethyl-m-tolamide Piperonyl butoxide	10	ASA	20:80	Fresh floral, rosewood
3-9	Polybutadiene-g-SAN	Citronellol	15	ABS	30:70	Mosquito-repellent effect
3-10	Polybutadiene-g-SAN	Citronellol	20	ABS	20:80	Repels/kills mosquitoes
3-11	Polybutadiene-g-SAN	Citronellol + clove powder 1:1	20	Polylactic acid	10:90	Fruity odor, lemon aroma
3-12	Denatured starch	Citronellol + clove powder 1:1	10	Polylactic acid	25:75	Fruity odor, repels small animals, dogs, cats
3-13	Denatured starch		15	Polylactic acid	20:80	Repels mosquitoes
3-14	Polylactic acid powder		10	Polyhydroxybutyrate-valerate copolymer	15:85	Fruity-spicy, repels mosquitoes and dogs

\* Chemical name in Table 3a

Table 3a:

Odorant BASF trade name	Chemical name
Linalyl acetate	3,7-Dimethyl-1,6-octadien-3-yl acetate
Isoamyl acetate	3-Methylbutyl acetate
Acetoin	3-Hydroxy-2-butanone
Tetrahydrolinalool	3,7-Dimethyloctan-3-ol

**Example 4:**

The version of the process described in this example, cold pressing, can be used for odorant oils which are particularly sensitive to high temperatures. The effect utilized here is that many plastics begin to flow under high pressure even below their melting point.

For this version of the process, the first polymer materials given in Table 4 were mixed with the odorant oils also given in Table 4 and allowed to swell until each odorant had become completely mixed into the first polymer material.

The second plastic used was the plastics given in Table 4, in the form of powder or fine regrind. Moldings were then pressed from this pulverulent mixture from 50 to 70°C under a pressure of 200 bar.

This process is particularly suitable for low-boiling pharmaceutically active substances, in particular naturally occurring substances. This version of the process is also highly suitable for the biodegradable polymers given in Examples 3-11 to 3-14 in Table 3, using the odorant oils which are also given in the table and are sensitive to high temperatures.

Table 4

No.	1st Polymer material	Odorant	% by weight	2nd Plastic	Mixing ratio polymer: plastic	Remarks
4-1	Polybutadiene-g-SAN	N,N-Diethyl-m-tolamide	12	SAN powder	40:60	Repels mosquitoes
4-2	Polybutadiene-g-SAN	Pheromone	2	ABS	20:80	Moth traps, attracts specific moths
4-3	Polybutadiene-g-SAN	Repellents	10	ABS	30:70	Repels dogs, cats
4-4	Polybutadiene-g-SAN	Pyrethrum extract + piperonyl butoxide	10	ABS	10:90	Insect poison
4-5	Polybutadiene-g-SAN	Chlorpyrifos	10	ABS	15:85	Moth agent
4-6	Polybutadiene-g-SAN	Azamethiphos	10	ABS	20:80	Attracts flies
4-7	Polybutadiene-g-SAN	Lavender oil	15	ABS	20:80	Lavender oil odor
4-8	Polybutadiene-g-SAN	Spruce needle oil	15	ABS	25:75	Spruce needle odor (odor dispenser)

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We claim:

1. A process for preparing odorant polymers or plastics, in which a comminuted or fine-particle first polymer material is mixed with a desired odorant, allowed to swell for a predetermined period, and, after being allowed to swell with the odorant, is mixed with a second plastic, where the first polymer material differs from the second plastic and is selected from particulate cross-linked plastics or from thermoplastic elastomers which have rubbery properties, with a glass transition temperature  $T_g$  of  $\leq 0^\circ\text{C}$ , which is below the glass transition temperature of the second plastic.
2. The process as claimed in claim 1, wherein the odorant used comprises an odorant oil.
3. A process as claimed in claim 1 or 2, wherein the odorant used comprises pheromones and/or ecomones.
4. A process as claimed in any of claims 1 to 3, wherein the first plastic is mixed and allowed to swell with the odorant in a closed container.
5. A process as claimed in any of claims 1 to 4, wherein the first polymer material in the form of a powder is mixed with the odorant, allowed to swell, and then further processed with the second plastic in ground, powder or pellet form under high pressure and at about room temperature, and with heating to a temperature which is below the glass transition temperature of the second plastic, or with heating to a temperature which is above the glass transition temperature either of the first polymer material or of the second plastic.

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6. A process as claimed in any of claims 1 to 5,  
wherein the first polymer material used comprises  
thermoplastics, thermoplastic elastomers, graft  
5 rubber, polymers based on renewable raw materials,  
or polymers or else polymer mixtures based on  
starch.
7. A process as claimed in claim 6, wherein the second  
10 plastic is selected from polylactic acid,  
polyurethanes, polyamides, polyesters, polyester-  
amides, and polybutylene terephthalates, or from  
polymers, copolymers, block copolymers, triblock  
15 copolymers, or graft copolymers of styrene,  
butadiene, acrylonitrile, (meth)acrylate, or of  
acrylic esters, and also mixtures of these with  
polycarbonates.
8. An odorant polymer or an odorant plastic obtained  
20 by the process as claimed in any of claims 1 to 7.
9. An odorant polymer or odorant plastic as claimed in  
claim 8 in pellet form.
- 25 10. The use of the odorant polymer or plastic as  
claimed in claim 8 or 9 for defense against  
animals.
- 30 11. A molding composition which comprises an odorant  
polymer or odorant plastic as claimed in claim 8 or  
9.
- 35 12. The use of the molding composition as claimed in  
claim 11 or of the odorant polymer or plastic as  
claimed in claim 8 or 9 for altering and/or  
improving the odor properties of articles.

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13. An article which comprises an odorant polymer or an odorant plastic as claimed in claim 8 or 9 and/or a molding composition as claimed in claim 11.

5 14. An article as claimed in claim 13 in the form of a plastic molding or a semifinished product.

15. The use of the article as claimed in claim 13 or 14 for improving room air quality.

10

16. The use of the article as claimed in claim 13 or 14 for defense against animal pests.

### Abstract

The invention relates to a process for preparing odorant polymers or plastics, in which a comminuted or fine-particle first polymer material is mixed with a desired odorant, allowed to swell for a predetermined period, and then further processed under a predetermined pressure and at a predetermined temperature. After the first polymer material has been allowed to swell with the odorant it may be mixed with a second plastic. The first polymer material and the second plastic may be identical or differ from one another.

The second plastic used in producing odorant polymers is also a polymer.

The invention further relates to the odorant polymer or odorant plastic prepared by the process of the invention, and to a molding composition or article which comprises the odorant polymer or the odorant plastic.



# Declaration, Power of Attorney

MAR 2001

09/762596

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0050/049256

We (I), the undersigned inventor(s), hereby declare(s) that:

My residence, post office address and citizenship are as stated below next to my name,

We (I) believe that we are (I am) the original, first, and joint (sole) inventor(s) of the subject matter which is claimed and for which a patent is sought on the invention entitled

Polymers and plastics with long-lasting odor and the use thereof

the specification of which

☐ is attached hereto.

☐ was filed on \_\_\_\_\_ as

Application Serial No. \_\_\_\_\_

and amended on \_\_\_\_\_.

☒ was filed as PCT international application

Number PCT/EP99/05703

on 06/08/1999

and was amended under PCT Article 19

on \_\_\_\_\_ (if applicable).

We (I) hereby state that we (I) have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

We (I) acknowledge the duty to disclose information known to be material to the patentability of this application as defined in Section 1.56 of Title 37 Code of Federal Regulations.

We (I) hereby claim foreign priority benefits under 35 U.S.C. § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed. Prior Foreign Application(s)

Application No.	Country	Day/Month/Year	Priority Claimed
19842203.2	Germany	07 August 1998	<input checked="" type="checkbox"/> Yes <input type="checkbox"/> No

**Declaration**

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(I) hereby claim the benefit under Title 35, United States Codes, § 119(e) of any United States provisional application(s) listed below.

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(Application Number)

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(Filing Date)

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(Application Number)

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(Filing Date)

We (I) hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s), or § 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

**Application Serial No.****Filing Date****Status (pending, patented,  
abandoned)**

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And we (I) hereby appoint **Messrs. HERBERT. B. KEIL**, Registration Number 18,967; and **RUSSEL E. WEINKAUF**, Registration Number 18,495; the address of both being Messrs. Keil & Weinkauf, 1101 Connecticut Ave., N.W., Washington, D.C. 20036 (telephone 202-659-0100), our attorneys, with full power of substitution and revocation, to prosecute this application, to make alterations and amendments therein, to sign the drawings, to receive the patent, and to transact all business in the Patent Office connected therewith.

We (I) declare that all statements made herein of our (my) own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

**Declaration**

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